

First-principles study of Ti-doped sodium alanate surfaces

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We have performed first-principles calculations of thick slabs of Ti-doped sodium alanate (NaAlH_4), which allows to study the system energetics as the dopant progresses from the surface to the bulk. Our calculations predict that Ti stays on the surface, substitutes for Na, and attracts a large number of H atoms to its vicinity. Molecular dynamics simulations suggest that the most likely product of the Ti-doping is the formation of H-rich TiAl_n ($n > 1$) compounds on the surface, and hint at the mechanism by which Ti enhances the reaction kinetics of NaAlH_4 .

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One key issue for the advancement of fuel-cell technologies is the development of safe and inexpensive ways of storing hydrogen aboard vehicles. In recent years sodium alanate (NaAlH_4) has become one of the most promising systems to achieve this goal. The kinetics of the reversible reaction by which pure NaAlH_4 releases hydrogen is relatively slow. However, it was discovered that a few percent of Ti doping increases the reaction rates dramatically [1], bringing the system close to what is required for practical applications. In spite of extensive investigations, the mechanism by which Ti enhances the reaction kinetics is still unknown [2, 3, 4]. In fact, even the location of the dopants, on the surface [5] or in the bulk of the system [4, 6], and the reactions they cause remain unclear. Some recent experimental results suggest the formation of a TiAl_3 compound on the surface of the system [7], but a consensus on this issue is yet to emerge.

In this Letter we present a theoretical study addressing the following outstanding questions. Where is Ti in doped NaAlH_4 , on the surface or in the bulk? If Ti stays on the surface, does it substitute for Na or Al, and what are the reactions and structural rearrangements it causes?

The calculations were performed within the generalized gradient approximation [8] to density functional theory as implemented in the code SIESTA [9]. We used a localized basis set including double- ζ and polarization orbitals, and Troullier-Martins pseudopotentials [10]. We tested the convergence of our calculations with respect to the k-point and real space meshes. For example, for the 001-surface calculations involving 4500 \AA^3 supercells and about 162 atoms, we used a $2 \times 2 \times 1$ k-point grid and a 150 Ry cutoff for the real space mesh. In our SIESTA calculations some accuracy is sacrificed, mainly because of the small basis set we use, so that bigger systems can be studied. Hence, we checked some representative SIESTA results with a more accurate *ab initio* method, using a plane-wave basis set and ultrasoft pseudopotentials [11] as implemented in the code CASTEP [12].

We started by determining which doping models of NaAlH_4 surfaces are most energetically favorable. For that purpose we considered the two slab-type supercells in Figs. 1a-b and 1c-d, which correspond to the most

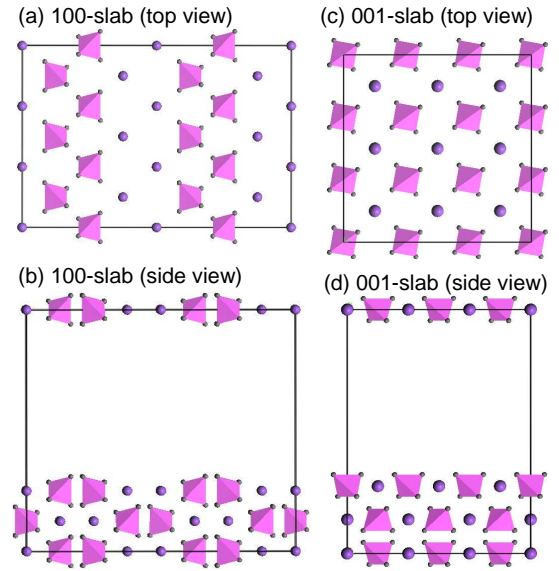


FIG. 1: Top and side views of the 100-slab (a-b) and the 001-slab (c-d) supercells of NaAlH_4 . Small and large gray spheres represent H and Na atoms, respectively. The Al atoms are at the center of the tetrahedra.

natural terminations of tetragonal NaAlH_4 [along the (100) and (001) directions, respectively]. Note that these supercells can be respectively regarded as composed of $3 \times 3 \times 4$ and $3 \times 3 \times 3$ NaAlH_4 groups (i.e., 216 and 162 atoms). In both cases we imposed that the atoms in the deepest layer be fixed at the bulk atomic positions, and allowed about 13 \AA of empty space between slabs. The bulk structural parameters ($a = b = 5.01 \text{ \AA}$ and $c = 11.12 \text{ \AA}$) were obtained from first-principles and are in good agreement with previously published results [13]. We considered a structure to be relaxed when residual force components are smaller than 0.03 eV/\AA . NaAlH_4 is a fairly ionic system [14, 15] and the pure surfaces do not present particularly relevant features. The electronic energy minimizations converge easily and the structural deviations from the bulk are relatively small.

In order to investigate the Ti doping of these surfaces, we computed the cohesive energy (E_{coh}) of a number of experimentally motivated doping models [13]: the sub-

TABLE I: Calculated cohesive energies, given in eV and per NaAlH_4 formula unit, for several doping models (see text). The column marked with an asterisk shows CASTEP results. In all the cases, E_{coh} of the pure surface is taken as the zero of energy. The pure E_{coh} values are given in the last line.

Doping model	(100)	(001)	(001)*
Ti @ Al	0.05	0.02	0.04
Ti @ Al + Na^v	-0.01	-0.09	-0.06
Ti @ Al + 2Na^v	-0.11	-0.28	-0.25
Ti @ Na	0.11	0.12	0.13
Ti @ Na + Na^v	0.04	0.03	0.04
Ti @ Na + 2Na^v	-0.01	-0.07	-0.05
undoped	20.48	19.28	20.15

stitution of Al and Na by Ti, as well as the occurrence of Na vacancies near the dopant. We use, for example, the notation “Ti@Na+ Na^v ” to refer to the case in which Ti substitutes for Na and there is a Na vacancy next to it. In all the calculations we considered only one Ti dopant in the supercell.

The cohesive energies shown in Table I were obtained as the sum of the individual atom energies minus the energy of the system. For both surfaces, E_{coh} of the pure case is taken as the zero of energy. Hence, the results in the table give minus the energy change in reactions of the form $\text{Ti} + \text{Na}_{27}\text{Al}_{27}\text{H}_{108} \rightarrow \text{Al} + \text{Na}_{27}\text{Al}_{26}\text{TiH}_{108}$, and measure the relative stability of pure and doped systems. A positive (and large) entry in the table indicates that, in principle, it is feasible to obtain the doped surface.

We find that both Ti@Na and Ti@Al are energetically more stable than the pure surfaces, i.e., the system gains energy by accepting a Ti dopant and releasing a Na or Al atom. In addition, Ti@Na is found to be the most favorable substitution, and the differences between the (100) and (001) surfaces are minor. Interestingly, the most favorable surface doping models turn out to be the same as in the bulk case [13]. We also find that the energy cost of forming Na vacancies is relatively small, suggesting they are likely to occur in the real doped system. Finally, Table I shows that the SIESTA and CASTEP results are in good agreement.

The obtained structural relaxations closely resemble those described in Ref. [13] for Ti-doped bulk NaAlH_4 . In the cases where Ti substitutes for Na, the dopant drags neighboring H atoms towards itself and greatly stretches the corresponding Al–H bonds. The Ti for Al substitution leads to an expansion of the TiH_4 group, as Ti is larger than Al. This size difference is probably the reason that Ti@Na has a larger cohesive energy than Ti@Al, even if the nominal valences of the atoms would suggest otherwise.

Next we studied whether the Ti dopant stays on the surface or, rather, penetrates into the bulk of the system. For that purpose, we considered slabs that are very thick

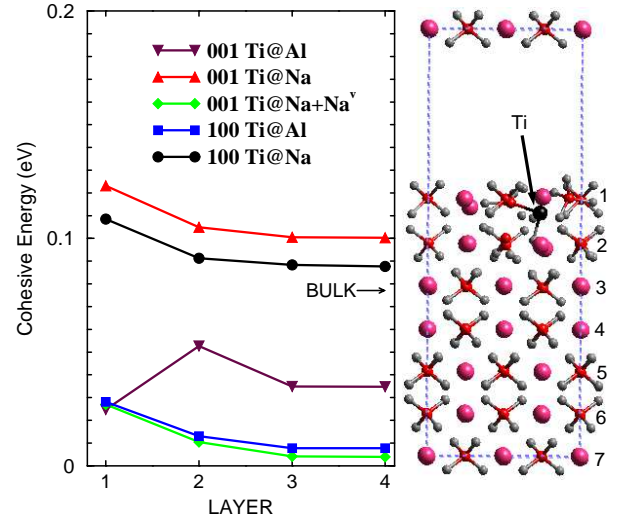


FIG. 2: Calculated cohesive energies of various doping models (see text) as a function of the Ti dopant location (see right panel). In all cases the pure surface E_{coh} is taken as the zero of energy.

along the direction normal to the surface (see Fig. 2), and computed the cohesive energy of the system as a function of the dopant position. More precisely, we worked with supercells formed by $7 \times 2 \times 2$ and $2 \times 2 \times 7$ NaAlH_4 groups, respectively, for the (100) and (001) surfaces. The atoms in the deepest layer are fixed at the bulk positions. Such supercells allow us to study the dopants up to three layers away from the surface, which we found is enough to reach the bulk limit. We focused on the doping models found to be more stable than the pure surface, i.e., Ti@Na, Ti@Al, and Ti@Na+ Na^v .

Figure 2 shows the results. In all cases E_{coh} of the pure system is subtracted so that the value at the surface approximately coincides with that of Table I. (The agreement between Table I and Fig. 2 should not be perfect, since the respective systems differ in dopant concentration.) Since a larger E_{coh} implies greater stability, we find that in all the cases considered it is energetically favorable for the Ti atom to remain on the surface of the system. In fact, the dopant always finds it favorable to locate in the outermost layer, except in the case of Ti@Al on the (001) surface.

As mentioned above, we find pure NaAlH_4 surfaces to be electronically and structurally similar to the bulk of the material. Hence, we think the dopants stay on the surface simply because this allows larger structural relaxations to accommodate them.

Finally, in an effort to understand better the reactions and structural relaxations that occur in real NaAlH_4 surfaces, we performed *ab initio* molecular dynamics (MD) simulations at 300 K. We worked with the (001) slab depicted in Fig. 1c-d and studied the doping models Ti@Na, Ti@Na+ Na^v , and Ti@Na+ 2Na^v . Our MD runs were about 2 ps long, which is hardly enough to thermalize

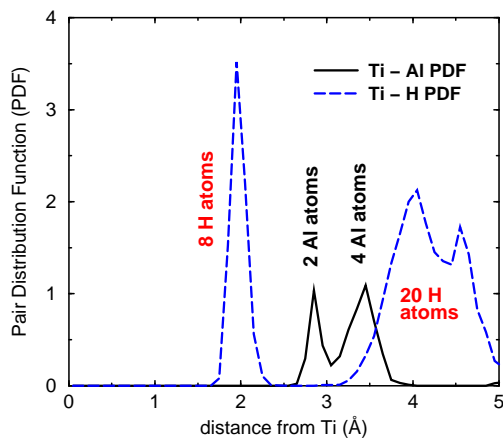


FIG. 3: Pair distribution function obtained from a 300 K *ab initio* MD simulation of the Ti@Na+2Na^v 001-surface (see text).

a system as reactive as this. Nevertheless, we were able to study the average bonding of Ti by calculating pair distribution functions (PDF's; Fig. 3 shows the result for Ti@Na+2Na^v), and reached two distinct conclusions.

In all the cases considered Ti is surrounded by a large number of H atoms. More precisely, the first Ti-H PDF peak is centered at about 1.9 Å and corresponds to 7 hydrogens for Ti@Na and 8 for Ti@Na+2Na^v, Ti@Na+Na^v being an intermediate case. These hydrogens travel continuously and freely between the dopant and the Al atoms they were originally bound to. The presence of the dopant thus results in a large number of loosely bound hydrogens that are relatively close to each other. This might well facilitate H₂ formation and release, consequently enhancing the kinetics of the reactions in the

decomposition/formation of doped alanates. Note that in Ref. [13] bulk Ti dopants were found to bind strongly a few H atoms at 0 K, and that is probably also the case for surface dopants. However, the dynamical situation at 300 K seems to be one in which *many* hydrogen atoms approach the dopant and none of them is actually tightly bound.

The other effect that we observed in all our MD runs is the formation of Ti-Al bonds. The first Ti-Al PDF peak is centered at about 2.75 Å and involves 2 Al atoms in the Ti@Na and Ti@Na+2Na^v cases, and almost 4 in the case of Ti@Na+Na^v. Taking into account that the typical Ti-Al distance in TiAl₃ systems is about 2.80 Å [16], this clearly hints at the formation of some kind of TiAl_n ($n > 1$) compound on the surface of the real material. The calculations suggest such a compound should be rich in interstitial hydrogen. Unfortunately, our supercells are not big enough to study the size and structure of these hypothetical TiAl_n compounds. Nevertheless, our results clearly support the conclusions of the recent X-ray absorption study of Ref. [7].

In summary, we have carried out a first-principles study of Ti-doped NaAlH₄ surfaces. Our conclusions are: (1) It is energetically favorable for the Ti dopants to stay on the surface rather than to penetrate into the bulk of the material. (2) Ti substitutes preferentially for Na, and formation of neighboring Na vacancies is likely. (3) The Ti dopant attracts to its neighborhood a large number of H atoms (up to 8). These hydrogens are loosely bound and close to each other, which might facilitate H₂ formation and release. (4) We find strong indications that a TiAl_n ($n > 1$) compound forms on the surface of the alanate, in support of recent experimental reports [7].

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